[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY AND CHEMOTHERAPY, EXPERIMENTAL BIOLOGY AND MEDICINE INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

# Relations between Rotatory Power and Structure in the Sugar Group. XXXVI.[1] The 1,5-Anhydrides of the Glycitols and Related Sugar Derivatives

BY HEWITT G. FLETCHER, JR., AND C. S. HUDSON

Twelve years ago, when Werner Freudenberg and E. F. Rogers[2] published their article on "the chemistry of naturally occurring monoanhydrohexitols" it had already been determined that polygalitol and styracitol are 1,5-anhydrides of D-mannitol and D-glucitol but it was not known which of these epimeric structures applies to each anhydride. Styracitol, to be sure, had been synthesized through the catalytic hydrogenation of tetraacetyl-2-hydroxy-D-glucal by Zervas[3] but this synthesis did not distinguish between the epimeric anhydrides since carbon atom two of tetraacetyl-2-hydroxy-D-glucal is symmetric. Freudenberg and Rogers obtained two indications that styracitol is of the D-mannitol series and polygalitol of the D-glucitol series. As the first of these indications, the rate of oxidation of styracitol by lead tetraacetate was found to be much faster than that of polygalitol, from which they inferred for styracitol the *cis*-relationship of hydroxyl groups on carbon atoms two and three that occurs in the 1,5-anhydro-D-mannitol configuration in contrast to the absence of such a pair of adjacent hydroxyl groups in the 1,5-anhydro-D-glucitol pattern; their inference was based upon the previous generalization by Criegee[4] that the *cis* arrangement is attacked more rapidly than is the *trans* by this type of selective oxidation. The second indication came from their comparison of optical rotatory values by the isorotation method. The pyranose (*i. e.*, 1,5-ring) substances of the D-glucose series are much more dextrorotatory than their epimers of the D-mannose series; thus the molecular rotation of methyl α-D-glucopyranoside is +30,860 and that of methyl α-D-mannopyranoside is +15,380, and the epimeric difference is thus 30,860 − 15,380 = +15,480, a large value. For polygalitol the molecular rotation is +6,950, for styracitol it is −8340 and the epimeric difference is +15,290. The closeness of the numerical agreement may possibly be fortuitous, since a comparison of the molecular rotations of methyl β-D-glucopyranoside (−6,640) and methyl β-D-mannopyranoside (−13,550) gives +6,910 for the epimeric difference. In either case, however, the comparison of rotations indicated in a qualitative way that polygalitol belongs in the D-glucose series and styracitol in the D-mannose series, on the assumption that the isorotation hypothesis applies to the substances with sufficient approximation to exclude an actual reversal of the sign of a large epimeric difference. These two agreeing indications that were noted by Freudenberg and Rogers have been shown by the later conclusive structural and configurational chemical proofs[5] to have led them to the correct assignment of configurations to polygalitol and styracitol. Since this example shows that the isorotation comparisons gave valuable early indications of configurations, we seek in the present article to extend such comparisons to a rather large group of sugar derivatives that are related through the common possession of a tetrahydropyrane structure, with particular emphasis on the 1,5-anhydroglycitols and their 2-desoxy derivatives, the hydroglycals.

Examination of Table I will demonstrate that the isorotation hypothesis holds well for the 1,5-anhydropentitols and for the four known 1,5-anhydrohexitols as well as for the fully acetylated derivatives of all these substances. The large epimeric differences of molecular rotation are of the correct sign throughout and they range in value between 5,500 and 7,650 for the 1,5-anhydrides and between 8,480 and 13,400 for the acetates of these anhydrides. In the hexitol series the 1,5-anhydrides of allitol, altritol, gulitol and iditol are still unknown; they constitute two epimeric pairs and its seems reasonable to predict that the epimeric difference for each pair will have the sign that is shown by the known pairs of Table I. If a member of one of these epimeric pairs should be discovered through a synthetic method that does not distinguish between epimers, as for example through the catalytic reduction of an acylated 2-hydroxyglycal, is it possible to assign the full configuration through the use of isorotation hypotheses? The answer to this question may be obtained through the following considerations.

The hydroglycal that is common to the D-glucose and D-mannose series (III) is closely related to polygalitol (I) and styracitol (II); it is a 2-desoxypolygalitol, which is synonymous with 2-desoxystyracitol. If the molecular rotation of polygalitol is expressed as B + A and that of styracitol as B − A, where A represents the contribution from carbon atom two and B that from the remainder of the structure, the molecular rotation of hydroglucal, in the structure of which carbon atom two is symmetric, may be written [(B + A) + (B − A)]/2 = B, if it be assumed that iso-

(1) Number XXXV, by W. T. Haskins, R. M. Hann and C. S. Hudson, was published in THIS JOURNAL, **69**, 1668 (1947).

(2) W. Freudenberg and E. F. Rogers, *ibid.*, **59**, 1602 (1937).

(3) L. Zervas, *Ber.*, **63**, 1689 (1930).

(4) R. Criegee, *Ann.*, **495**, 211 (1932); **507**, 159 (1933).

(5) (a) L. Zervas and I. Papadimitriou, *Ber.*, **73**, 174 (1940); (b) N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **65**, 64 (1943); (c) N. K. Richtmyer, C. J. Carr and C. S. Hudson, *ibid.*, **65**, 1477 (1943); (d) R. C. Hockett and Maryalice Conley, *ibid.*, **66**, 464 (1944).

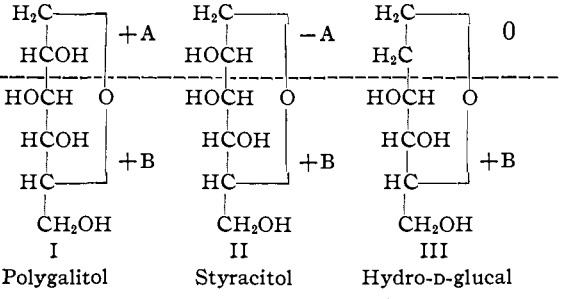
TABLE I

PROPERTIES OF 1,5-ANHYDROGLYCITOLS DERIVED FROM MONOSACCHARIDES

| | Formula | $C_2$–OH (or OAc) group | M. p., °C. | Mol. wt. | $[\alpha]^{20}D$ | Solvent | $[M]^{20}D$ | $B$ | $B_{Ac}$ |
|---|---|---|---|---|---|---|---|---|---|
| **4-Desoxypentitol Series** | | | | | | | | | |
| 1,5-Anhydro-D-*threo*-4-desoxypentitol[a] | XV | – | 67–68[b] | 118 | −44.9[b] | $H_2O$ | − 5,300 | 5500 | |
| 1,5-Anhydro-D-*erythro*-4-desoxypentitol[a] | XI | + | Amorph.[c] | 118 | +48.2[c] | $H_2O$ | + 5,690 | | |
| Diacetate of XV | | – | Amorph.[b] | 202 | −38.8[b] | $C_2H_5OH$ | − 7,840 | | 8,480 |
| Diacetate of XI | | + | Amorph.[d] | 202 | +45.1[d] | $CHCl_3$ | + 9,110 | | |
| **Pentitol Series** | | | | | | | | | |
| 1,5-Anhydro-D-arabitol | XVII | – | 96–97[e] | 134 | −98.6[e] | $H_2O$ | −13,200 | 6600 | |
| 1,5-Anhydroribitol | XIX | + | 128–129[f] | 134 | 0 (*meso*) | | 0 | | |
| Triacetate of XVII | | – | 58[e] | 260 | −74.2[e] | $CHCl_3$ | −19,300 | | 9,660 |
| Triacetate of XIX | | + | 133–134[f] | 260 | 0 (*meso*) | | 0 | | |
| 1,5-Anhydro-D-lyxitol[a] | XVII | – | 96–97[e] | 134 | −98.6[e] | $H_2O$ | −13,200 | 6600 | |
| 1,5-Anhydroxylitol | XVI | + | 116–117[g] | 134 | 0 (*meso*) | | 0 | | |
| Triacetate of XVII | | – | 58[e] | 260 | −74.2[e] | $CHCl_3$ | −19,300 | | 9,660 |
| Triacetate of XVI | | + | 122[g] | 260 | 0 (*meso*) | | 0 | | |
| **Hexitol Series** | | | | | | | | | |
| 1,5-Anhydro-D-mannitol | II | – | 155[h] | 164 | −50.9[h] | $H_2O$ | − 8,340 | 7650 | |
| 1,5-Anhydro-D-glucitol | I | + | 141–142[i] | 164 | +42.4[i] | $H_2O$ | + 6,950 | | |
| Tetraacetate of II | | – | 66–67, 58[j] | 332 | −42.0[k] | $CHCl_3$ | −13,900 | | 13,400 |
| Tetraacetate of I | | + | 73–74[l] | 332 | +38.9[l] | $CHCl_3$ | +12,900 | | |
| 1,5-Anhydro-D-talitol | VI | – | Amorph.[m] | 164 | −11.4[m] | $H_2O$ | − 1,870 | 7240 | |
| 1,5-Anhydro-D-galactitol | VII | + | 114[n] | 164 | +76.6[n] | $H_2O$ | +12,600 | | |
| Tetraacetate of VI | | – | 106–107[m] | 332 | −16.2[m] | $CHCl_3$ | − 5,380 | | 10,800 |
| Tetraacetate of VII | | + | 75–76[n] | 332 | +49.1[n] | $CHCl_3$ | +16,300 | | |

[a] The names of XV, XI and XVII are systematic alternative designations of the known hydro-D-xylal, hydro-L-arabinal and 1,5-anhydro-D-arabitol. [b] M. Gehrke and F. Obst, *Ber.*, **64**, 1724 (1931). [c] G. E. Felton and W. Freudenberg, THIS JOURNAL, **57**, 1637 (1935). [d] See text of present paper and also M. Gehrke and F. X. Aichner, *Ber.*, **60**, 918 (1927). [e] H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **69**, 1672 (1947). [f] R. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **70**, 4052 (1948). [g] H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **69**, 921 (1947). [h] R. C. Hockett and Maryalice Conley, *ibid.*, **66**, 464 (1944). [i] N. K. Richtmyer and C. S. Hudson, *ibid.*, **65**, 64 (1943). [j] Y. Asahina, *Ber.*, **45**, 2363 (1912). [k] This hitherto unpublished value was obtained in this Laboratory using a concentration of 2.634 g. per 100 ml. of solution. Asahina (*loc. cit.*) reported a rotation of −20.9° in alcohol. [l] N. K. Richtmyer, C. J. Carr, Jr., and C. S. Hudson, THIS JOURNAL, **65**, 1477 (1943). [m] D. A. Rosenfeld, N. K. Richtmyer and C. S. Hudson, *ibid.*, **70**, 2201 (1948). [n] H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **70**, 310 (1948).

rotation holds for the three substances. Even though it cannot be expected that it will hold with




mathematical precision, it may be that the approximation will be such that the molecular rotation of hydroglucal will lie well between those of polygalitol and styracitol. Such is indeed the case, as is shown by the data in Tables I and III; polygalitol (+6,950), hydro-D-glucal (+2,440) and styracitol (−8,340). Likewise the molecular rotation of hydro-D-arabinal (−5,690) lies between those for 1,5-anhydro-D-arabitol (−13,200) and 1,5-anhydroribitol (0), the molecular rotation of hydro-D-xylal (−5,300) lies between those for 1,5-anhydro-D-lyxitol (synonym, 1,5-anhydro-D-arabitol) (−13,200) and 1,5-anhydroxylitol (0) while the molecular rotation of hydro-D-galactal (+7,120) is between those for 1,5-anhydro-D-talitol (−1,870) and 1,5-anhydro-D-galactitol (+12,600). As is to be expected, the molecular rotations of those acetates of these compounds that are known are similarly related. Thus triacetylhydro-D-glucal has a molecular rotation (+9,750) which is between the values for tetraacetylstyracitol (−13,900) and tetraacetylpolygalitol (+12,900); in the five-carbon series the molecular rotation of diacetylhydro-D-xylal (−7,840) is seen to lie between those for triacetyl-1,5-anhydro-D-lyxitol (synonym, triacetyl-1,5-anhydro-D-arabitol) (−19,300) and triacetyl-1,5-anhydroxylitol (0).

The literature reveals that an amorphous diacetylhydroarabinal having a dextrorotation in

TABLE II

PROPERTIES OF THE SUBSTITUTED 1,5-ANHYDROGLYCITOLS DERIVED FROM THE DISACCHARIDES

| | Formula | $C_2$–OH (or OAc) group | M. p. | Mol. wt. | $[\alpha]^{20}D$ | Solvent | $[M]D$ |
|---|---|---|---|---|---|---|---|
| 1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol (= 1,5-anhydrocellobiitol) | VIII | + | 172[a] | 326 | + 29.3[a] | $H_2O$ | + 9,550 |
| Heptaacetate of VIII | | + | 75–76[a] | 621 | + 4.0[a] | $CHCl_3$ | + 2,500 |
| 1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol (= 1,5-anhydrogentiobiitol) | XXI | + | 239–240[a] | 326 | + 3.6[a] | $H_2O$ | + 1,200 |
| Heptaacetate of XXI | | + | 153[a] | 621 | + 13.0[a] | $CHCl_3$ | + 8,070 |
| 1,5-Anhydro-4-(β-D-galactopyranosyl)-D-glucitol (= 1,5-anhydrolactitol) | XII | + | 233–237 (dec.)[b] | 326 | + 49.4[b] | $H_2O$ | +16,100 |
| 1,5-Anhydro-4-(α-D-glucopyranosyl)-D-glucitol (= 1,5-anhydromaltitol) | XIII | + | Amorph.[b] | 326 | +132[b] | $H_2O$ | +43,000 |
| Heptaacetate of XIII | | + | 133–134[b] | 621 | + 82.0[b] | $CHCl_3$ | +50,900 |

[a] H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **70**, 310 (1948). [b] H. G. Fletcher, Jr., L. H. Koehler and C. S. Hudson, *ibid.*, **71**, 3679 (1949).

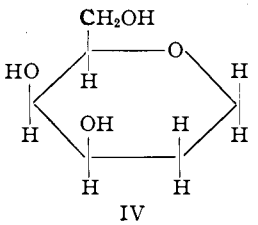
TABLE III

PROPERTIES OF THE HYDROGLYCALS (1,5-ANHYDRO-2-DESOXYGLYCITOLS)

| | Formula | M. p., °C. | Mol. wt. | $[\alpha]D$ | Solvent | $[M]D$ |
|---|---|---|---|---|---|---|
| Hydro-D-arabinal[a] | XVIII | Amorph.[a] | 118 | −48.2[a] | $H_2O$ | −5690 |
| Diacetate of XVIII[b] | | Amorph.[b] | 202 | −45.1[b] | $CHCl_3$ | −9110 |
| Hydro-D-xylal | XV | 67–68[c] | 118 | −44.9[c] | $H_2O$ | −5300 |
| Diacetate of XV | | Amorph.[c] | 202 | −38.8[c] | $C_2H_5OH$ | −7840 |
| Hydro-D-glucal | III | 86–87[d] | 148 | +16.5[d] | $H_2O$ | +2440 |
| Triacetate of III | | Amorph.[e] | 274 | +35.6[e] | $C_2H_5OH$ | +9750 |
| Hydro-D-galactal | IV | 128[d] | 148 | +48.1[c] | $H_2O$ | +7120 |
| 4-(β-D-Glucopyranosyl)-hydro-D-glucal (hydrocellobial) | IX | 222[f] | 310 | + 4.5[f] | $H_2O$ | +1400 |
| Hexaacetate of IX | | 133–134[f] | 563 | +11.2[f] | $C_2H_4Cl_2$ | +6310 |
| 6-(β-D-Glucopyranosyl)-hydro-D-glucal (hydrogentiobial) | XX | ..... | 310 | −10.2[g] | $H_2O$ | −3160 |
| Hexaacetate of XX | | 132–133[g] | 563 | +11.8[g] | $C_5H_5N$ | +6640 |
| 4-(β-D-Galactopyranosyl)-hydro-D-glucal (hydrolactal) | XIV | 204–205[h] | 310 | +28.6[h] | $H_2O$ | +8800 |

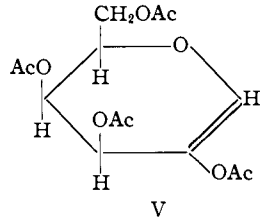
[a] Hydro-D-arabinal has not been reported; its enantiomorph was made by G. E. Felton and W. Freudenberg, THIS JOURNAL, **57**, 1637 (1935), and, with changed sign, we use here the rotational value reported by these authors. [b] See text of present paper and also M. Gehrke and F. X. Aichner, *Ber.*, **60**, 918 (1927). [c] M. Gehrke and F. Obst, *ibid.*, **64**, 1724 (1931). [d] H. Lohaus and O. Widmaier, *Ann.*, **520**, 301 (1935). [e] E. Fischer, *Ber.*, **47**, 196 (1914). [f] E. Fischer and K. von Fodor, *ibid.*, **47**, 2057 (1914). [g] M. Bergmann and W. Freudenberg, *ibid.*, **62**, 2783 (1929). [h] E. Fischer and G. O. Curme, Jr., *ibid.*, **47**, 2047 (1914).

chloroform of +43.1° was reported by Gehrke and Aichner.[6] These authors, however, failed to state to which series (D or L) their substance belonged and internal evidence was lacking since both D- and L-arabinose derivatives are reported elsewhere in the same paper; the present authors have therefore repeated this preparation. Diacetyl-D-



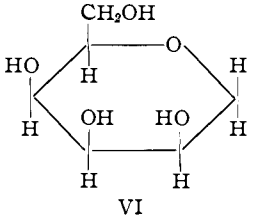
IV

Hydro-D-galactal
$[M]_D$ +7,120



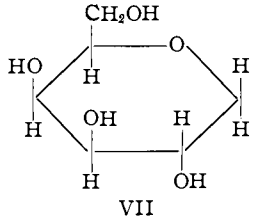
V

Tetraacetyl-2-hydroxy-D-galactal



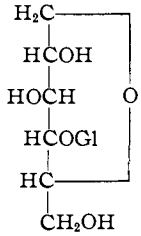
VI

1,5-Anhydro-D-talitol
$[M]_D$ −1,870



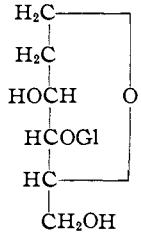
VII

1,5-Anhydro-D-galactitol
$[M]_D$ +12,600



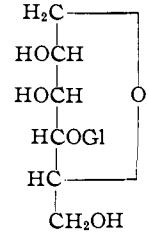
VIII

1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol
$[M]_D$ = +9550
(Gl = β-D-glucopyranosyl)



IX

Hydrocellobial
$[M]_D$ = +1400



X

1,5-Anhydro-4-(β-D-glucopyranosyl)-D-mannitol
(unknown)

(6) M. Gehrke and F. X. Aichner, *Ber.*, **60**, 918 (1927).

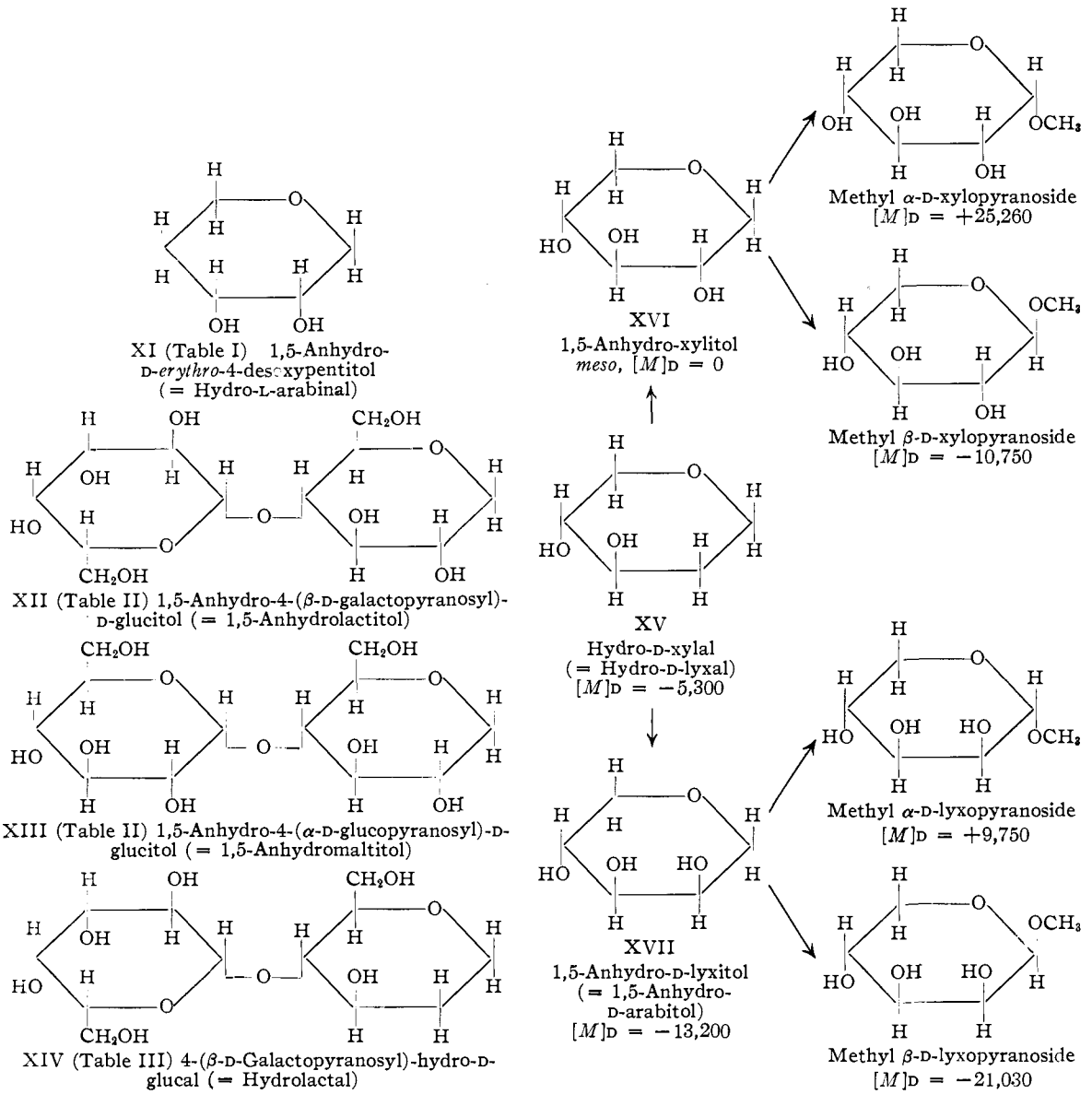



Fig. 1.—Some rotatory relations in the D-xylose and D-lyxose series.

arabinal, prepared from 2,3,4-triacetyl-D-arabinosyl bromide in 66% yield according to the method of Karrer and co-workers[7] was hydrogenated, following the directions of Gehrke and Aichner,[6] to give in 86% yield diacetylhydro-D-arabinal as a colorless, viscid liquid boiling at 0.2 mm. pressure at 90° and having $n^{20}D$ 1.4523. The specific rotation of this substance, $[\alpha]^{20}D$, in chloroform was found to be −45.1° (*c*, 3.02) and it is therefore evident that the product having a rotation of +43.1° reported by Gehrke and Aichner was diacetylhydro-L-arabinal. In agreement with the examples cited above the molecular rotation of diacetylhydro-D-arabinal (−9,110) lies well between those of the two corresponding 1,5-anhydropentitol acetates, triacetyl-1,5-anhydro-D-arabitol (−19,300) and triacetyl-1,5-anhydroribitol (0).

This relationship between the molecular rotations of a hydroglycal and its two corresponding 1,5-anhydroglycitols thus appears to be a general one in a qualitative way and it may be said that *although the molecular rotation of a hydroglycal is not the exact mathematical average of those of the corresponding epimeric 1,5-anhydroglycitols, it lies well between their greatly differing values.*

If this generalization had been known at an earlier date, which was not possible because the pertinent data upon which it is founded were not then known, one could have inferred that the 1,5-anhydrohexitol which Freudenberg and Rogers[2]

(7) P. Karrer, B. Becker, F. Benz, P. Frei, H. Salomon and K. Schöpp, *Helv. Chim. Acta*, **18**, 1435 (1935).

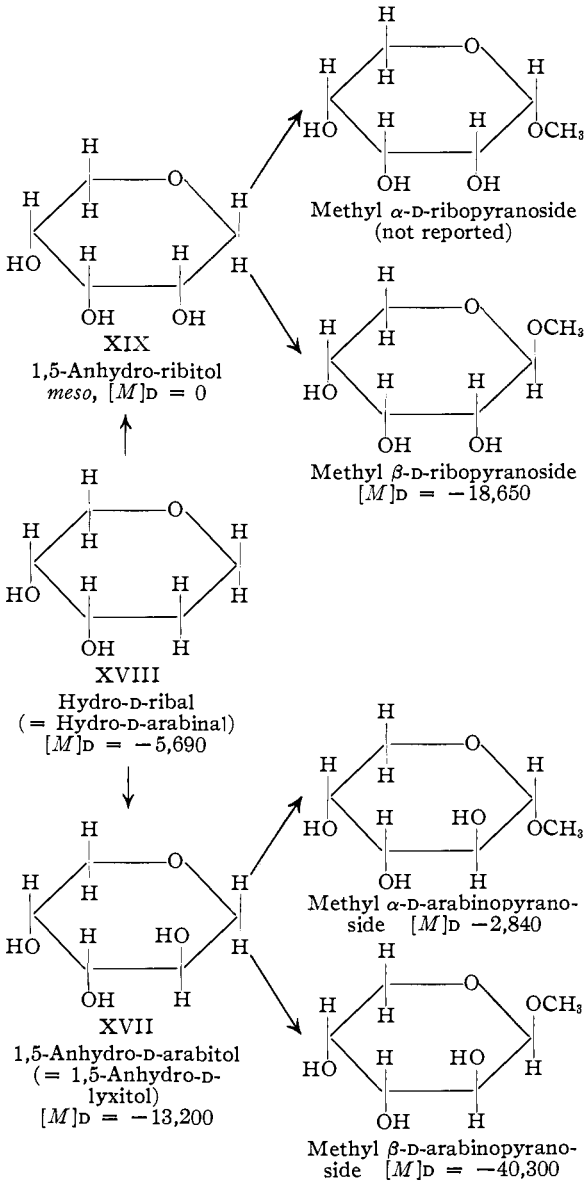



Fig. 2.—Some rotatory relations in the D-ribose and D-arabinose series.

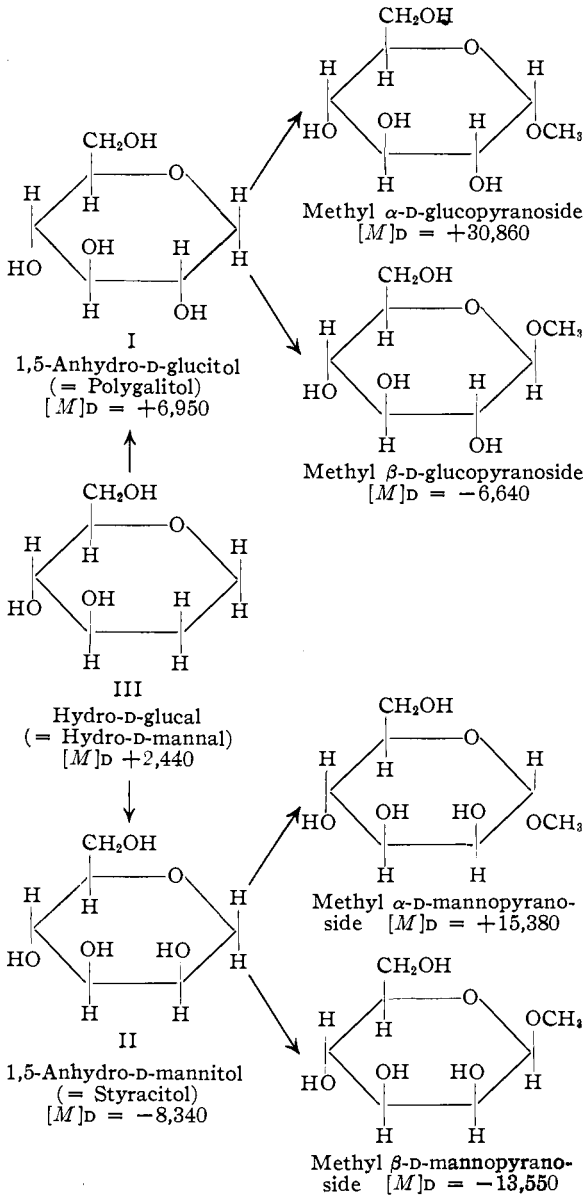



Fig. 3.—Some rotatory relations in the D-glucose and D-mannose series.

synthesized through the catalytic reduction of tetraacetyl-2-hydroxy-D-galactal (IV) was of the D-talitol rather than D-galactitol series since the 1,5-anhydroglycitol which these authors obtained had a molecular rotation of −1,870 and was thus more levorotatory than hydro-D-galactal (IV) (+7,120). Actual proof of the configuration of the substance in question as 1,5-anhydro-D-talitol finally came through unequivocal independent syntheses of 1,5-anhydro-D-talitol[8] and 1,5-anhydro-D-galactitol.[9]

From the above it is apparent that should the catalytic reduction of an acetylated 2-hydroxyglycal ever give rise to both of the expected 1,5-anhydroglycitols[10] each of the two substances may at once be assigned its proper configuration, solely on the basis of its rotation and without recourse to comparison with the rotation of the corresponding hydroglycal.

The foregoing discussion has been limited to derivatives of the monosaccharides; those of some

(8) D. A. Rosenfeld, N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **70**, 2201 (1948).

(9) H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **70**, 310 (1948).

(10) The palladium-catalyzed reduction of tetraacetyl-2-hydroxy-D-glucal has, for instance, been shown (ref. 5c) to produce a small quantity of 1,5-anhydro-D-glucitol although 1,5-anhydro-D-mannitol is the predominating product. Hockett and Conley (ref. 5d) have indicated that the nature of the catalyst employed may influence the proportions of products formed.

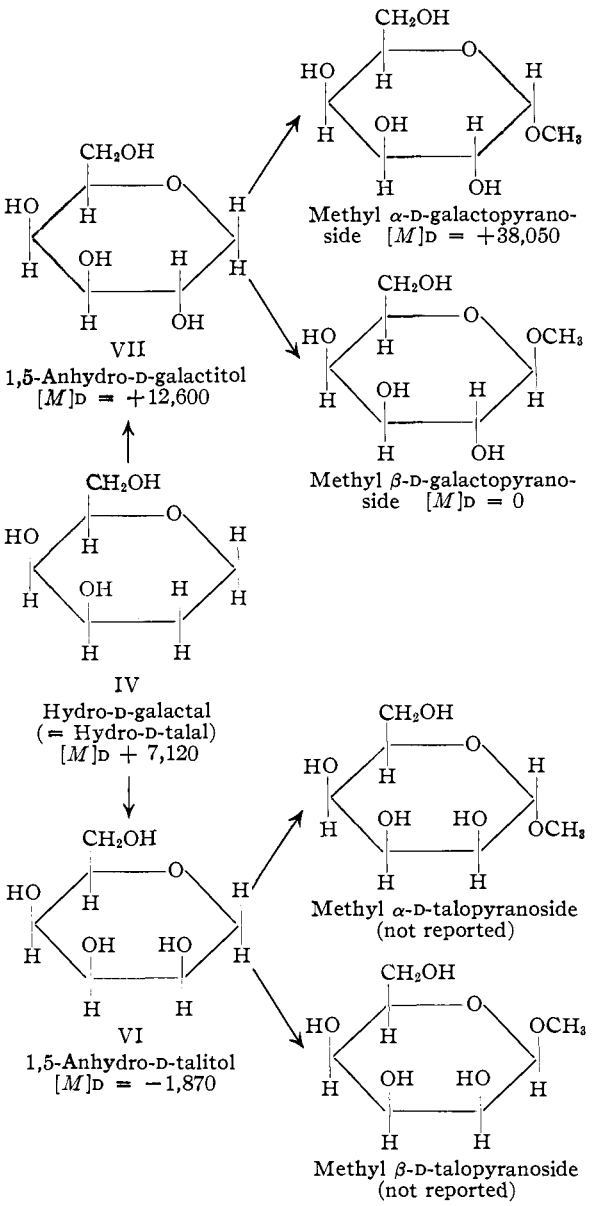



Fig. 4.—Some rotatory relations in the D-galactose and D-talose series.

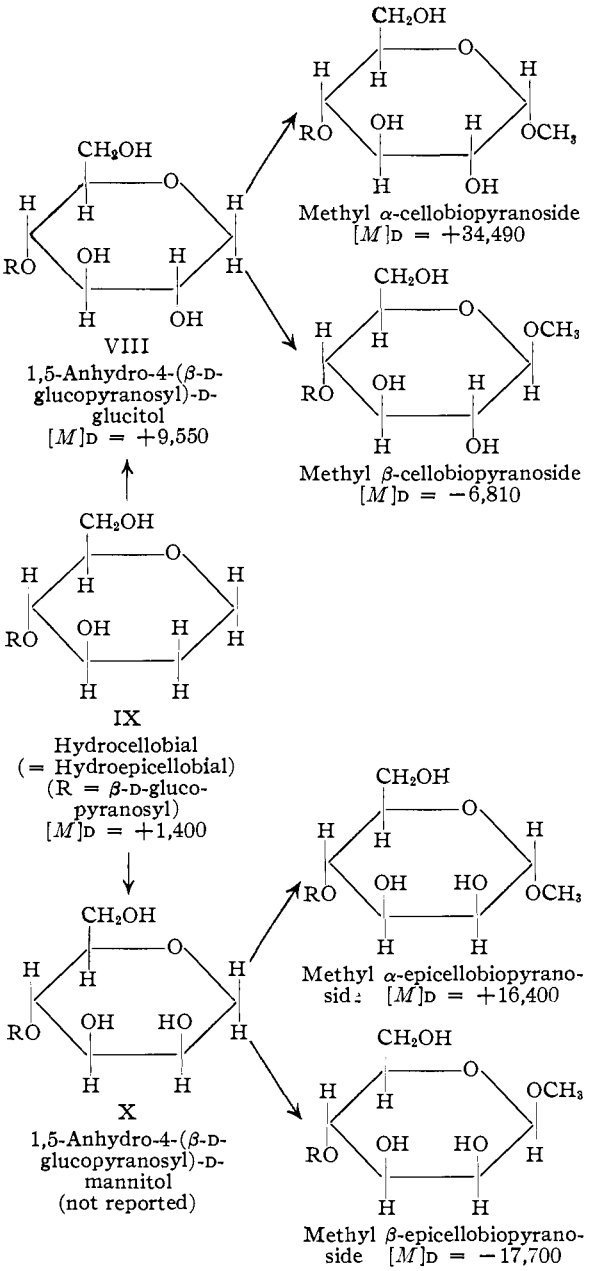



Fig. 5.—Some rotatory relations in the cellobiose and epicellobiose series.

disaccharides will now be considered. In no case are data now known for an epimeric pair of the pertinent 1,5-anhydro derivatives. The hydroglycals from cellobiose, gentiobiose and lactose were synthesized many years ago; the data concerning them are shown in Table II. Maurer and Plötner[11] synthesized 1,5-anhydro derivatives in the cellobiose and gentiobiose series through the palladium-catalyzed reduction of the respective heptaacetyl-2-hydroxyglycals, and though they designated these anhydrides as substituted styracitols (*i. e.*, as derivatives of D-mannitol by present knowledge) it is apparent that there was no just basis for excluding the possibility that they were substituted polygalitols. Indeed, a consideration of the pertinent rotatory relations as developed previously in this article leads clearly to the inference that these two 1,5-anhydro derivatives, one from cellobiose and one from gentiobiose, are substituted polygalitols. In each case the substituted 1,5-anhydride is more dextrorotatory than the corresponding hydroglycal (see Tables II and III), just as polygalitol is more dextrorotatory than hydro-D-glucal. All doubt concerning the allocations has been removed lately through the syn-

(11) K. Maurer and K. Plötner, *Ber.*, **64**, 281 (1931).

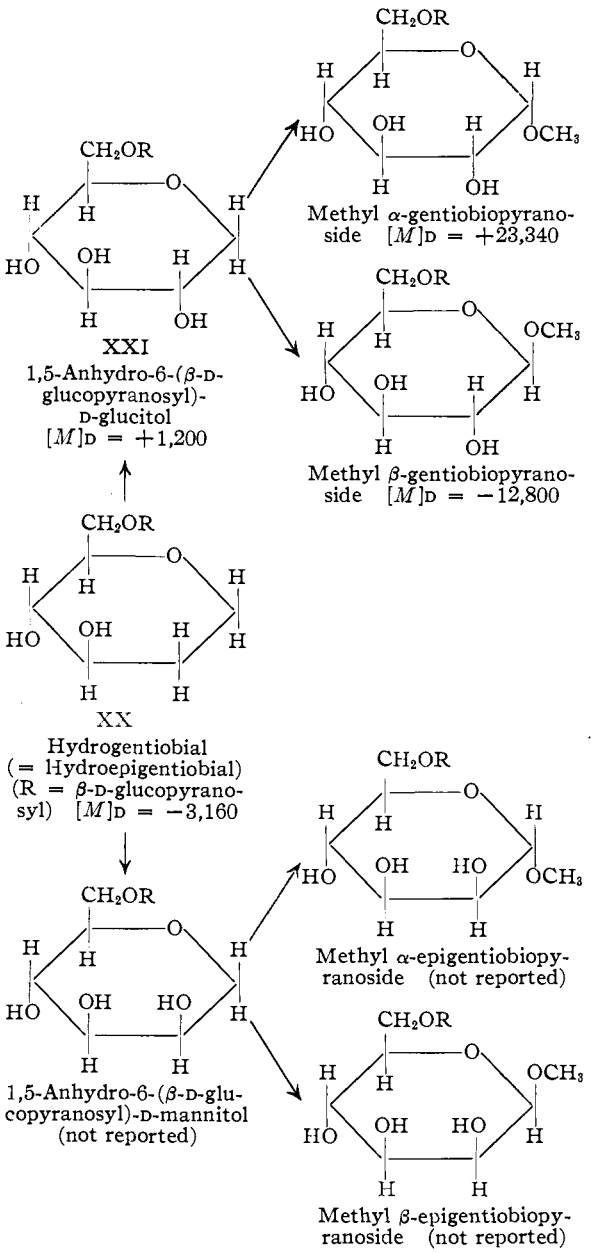



Fig. 6.—Some rotatory relations in the gentiobiose and epigentiobiose series.

thesis of authentic 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol by the reductive desulfurization of phenyl 1-thio-β-cellobioside heptaacetate and of 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol from phenyl 1-thio-β-gentiobioside heptaacetate in like manner.[9] The substances proved to be identical with those discovered by Maurer and Plötner; they are substituted polygalitols rather than substituted styracitols.

The recent preparation of an anhydride in the lactose series, 1,5-anhydro-4-(β-D-galactopyranosyl)-D-glucitol[12] affords an analogous example; as will be seen from Tables II and III the anhydride (+16,100), a substituted polygalitol, is more dextrorotatory than the long known hydrolactal (+8,800).

With the data which are available in Tables I, II and III, and assuming isorotation, it is possible to predict the sign and order of magnitude of the rotations of some 1,5-anhydrides which have not as yet been reported. Thus, using the molecular rotation of the known 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol (+9,550) and the molecular rotation of hydrocellobial (+1,400), it is simple to calculate the molecular rotation of the unknown epimeric anhydride, 1,5-anhydro-4-(β-D-glucopyranosyl)-D-mannitol, as 2 × 1,400–9,550 = −6,750, corresponding to a specific rotation of −21°. Alternatively, the difference between the epimers polygalitol and styracitol (+6,950 − (−8,340) = +15,290) may be used to calculate a value of 9,550 − 15,290 = −5,740, corresponding to a specific rotation of −17° for the same anhydride.

Attention is next directed to the Figs. 1–6.[13] In the left hand column of each of these figures one will observe that the arrangements portray the relationship that has been shown between the molecular rotation of a hydroglycal and those of the members of the related epimeric pair of 1,5-anhydroglycitols. An inspection of the two combined columns of these figures leads to a new generalization which may be stated as follows: *the molecular rotation of a 1,5-anhydroglycitol lies well between the molecular rotations of the anomeric methyl glycopyranosides of the corresponding aldose.* Each methyl α-D-glycopyranoside is much more dextrorotatory, and each methyl β-D-glycopyranoside is much more levorotatory, than the corresponding 1,5-anhydro-D-glycitol. This generalization is not a purely empirical one; it has the same type of basis upon the isorotation hypothesis as does the relationship between the rotation of a hydroglycal and the corresponding 1,5-anhydroglycitol. From Figs. 1–6 it will be seen that the molecular rotation of a 1,5-anhydroglycitol is not the exact mathematical mean of the molecular rotations of the corresponding methyl glycopyranosides but that it does lie so well between them that the generalization can be applied without uncertainty.

## Summary

Some relationships between molecular rotation and configuration among the hydroglycals, the 1,5-anhydroglycitols and the methyl glycopyranosides have been pointed out.

BETHESDA, MARYLAND RECEIVED MAY 5, 1949

(12) H. G. Fletcher, Jr., L. H. Koehler and C. S. Hudson, THIS JOURNAL, **71**, 3679 (1949).

(13) The molecular rotations of the methyl glycopyranosides in Figs. 1 to 6 have been taken from the book by F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," U. S. Govt. Printing Office, Washington, D. C., 1942.